

TABLE II. PREPARATION OF STABLE ACRYLIC RESIN EMULSIONS<sup>a</sup>

Expt. No.	Designation	Emulsifier	Type	Grams	Other Agents, Grams	Water, Ml.	Methyl acrylate	Monomers, Ml. Acrylonitrile	Catalyst, Ml.	Time, Min.	Films
1	E. F. Houghton No. 1			0.9	0.9 NH <sub>4</sub> Alg. <sup>b</sup>	60	50		H <sub>2</sub> O <sub>2</sub> , 1	150	Smooth, flexible, clear
2	E. F. Houghton No. 1			4.0	4.0 NH <sub>4</sub> Alg.	250	200	50	H <sub>2</sub> O <sub>2</sub> , 3	200	Same
3	E. F. Houghton No. 1			4.0	4.0 NH <sub>4</sub> Alg.	250	225	25	H <sub>2</sub> O <sub>2</sub> , 2	135	Same
4	E. F. Houghton No. 1			0.5	0.7 NH <sub>4</sub> Alg.	35	45		H <sub>2</sub> O <sub>2</sub> , 0.5	65	Same
5	E. F. Houghton No. 1			0.5	0.7 NH <sub>4</sub> Alg.	35	45	5.0 <sup>c</sup>	cc.	90	Same
6	E. F. Houghton No. 1			0.9	0.7 NH <sub>4</sub> Alg.	55	45		H <sub>2</sub> O <sub>2</sub> , 1	105	Cloudy; re-emulsifies in water
7	Naeconol NRSF		Sodium alkyl aryl sulfonate	0.9	0.7 NH <sub>4</sub> Alg.	55	45		H <sub>2</sub> O <sub>2</sub> , 1	75	Clear; becomes soapy in water
8	Sulfonated castor oil			0.9	0.7 NH <sub>4</sub> Alg.	55	45		H <sub>2</sub> O <sub>2</sub> , 0.5	110	Clear and colorless
9	Tergitol Penetrant No. 4		Na salt of higher sec alkyl sulfate	0.9	0.5 NH <sub>4</sub> Alg.	53	45		H <sub>2</sub> O <sub>2</sub> , 0.5	135	Same; turns white
10	Aqual-AR-75%			0.9	0.5 NH <sub>4</sub> Alg.	50	45		H <sub>2</sub> O <sub>2</sub> , 1	150	Same
11	Aqual-AR-75%			0.5	0.3 NaOH	50	40		H <sub>2</sub> O <sub>2</sub> , 3	125	Same
12	Daktose		Decacetylated chitin	0.8	Buffer (pH 8.95) 5 cc.	60	40	1.0 <sup>c</sup>	H <sub>2</sub> O <sub>2</sub> , 0.75	45	Opaque, nontacky
13	Daktose			5.0	Acetic acid 1.0	60	35		H <sub>2</sub> O <sub>2</sub> , 0.5	30	Same
14	Aqual-AR-75%			5.0	Acetic acid 0.5	500	500		H <sub>2</sub> O <sub>2</sub> , 2.5	45	Smooth, clear
15	Aqual-AR-75%			5.0	Buffer 8 cc.	500	450	50	H <sub>2</sub> O <sub>2</sub> , 4	95	Colorless, nontacky, tough
16	Aqual-AR-75%			5.0	5.0 NaOH	500	400		Liquidol, 0.5 g.	155	Hard, brittle
17	Aqual-AR-75%			5.0	5.0 NaOH	500	400	100	H <sub>2</sub> O <sub>2</sub> , 4	210	Same
18	Aqual-AR-75%			5.0	5.0 NaOH	500	400	100	H <sub>2</sub> O <sub>2</sub> , 2	195	Hard and tough, not brittle
19	E. F. Houghton No. 1			5.0	7.0 NH <sub>4</sub> Alg.	500	450	110	H <sub>2</sub> O <sub>2</sub> , 0.5	180	Smooth, clear, tough, nontacky
20	E. F. Houghton No. 1			5.0	7.0 NH <sub>4</sub> Alg.	500	450	50	H <sub>2</sub> O <sub>2</sub> , 1	60	Smooth, clear
21	E. F. Houghton No. 1			0.9	0.9 NH <sub>4</sub> Alg.	60	500		H <sub>2</sub> O <sub>2</sub> , 2.5	150	Same
22	E. F. Houghton No. 1			0.9	0.9 NH <sub>4</sub> Alg.	60	50		H <sub>2</sub> O <sub>2</sub> , 0.5	150	Same
23	E. F. Houghton No. 1			0.7	0.5 NH <sub>4</sub> Alg.	20	45		H <sub>2</sub> O <sub>2</sub> , 1	150	Same
24	E. F. Houghton No. 1			0.7	0.5 NH <sub>4</sub> Alg.	20	45		H <sub>2</sub> O <sub>2</sub> , 0.25	150	Same
25	Triton-K80-S		Quaternary ammonium salt	0.9	0.8	60	20		Liquidol, 0.5 g.	90	Smooth
26	Daktose			0.4	Acetic acid 0.5	500	45		Liquidol, 1.5 g.	45	Smooth
27	Aqual-AR-75%			8.0	3.0 NH <sub>4</sub> Alg.	500	45		H <sub>2</sub> O <sub>2</sub> , 2	30	Opaque, nontacky
28	E. F. Houghton No. 1			1.0	Pectinate H-49/	82	40		H <sub>2</sub> O <sub>2</sub> , 2	90	Smooth, clear
29	E. F. Houghton No. 1			1.0	Protovac 8979 <sup>d</sup>	70	450	50	H <sub>2</sub> O <sub>2</sub> , 1.5	95	Adheres to glass; slightly cloudy
30	Aqual-AR-75%		Sodium alkyl naphthalene sulfonate	1.0	Pectinate H-49/	70	50		H <sub>2</sub> O <sub>2</sub> , 0.5	95	Rough, irregular
31	Nekal-BX			1.0	Protovac 8979 <sup>d</sup>	280	50		H <sub>2</sub> O <sub>2</sub> , 0.2	13	Adheres to glass; slightly cloudy
32	Tergitol Penetrant No. 4			4.0	Protovac 8979 <sup>d</sup>	70	50		H <sub>2</sub> O <sub>2</sub> , 0.1	35	Same
33	Tergitol Penetrant No. 4			1.0	Protovac 8979 <sup>d</sup>	50	225		H <sub>2</sub> O <sub>2</sub> , 0.2	26	Adheres to glass; slightly cloudy
34	E. F. Houghton No. 1		Dioctyl ester of sodium sulfosuccinic acid	0.5	0.7 Morpholine	50	50		H <sub>2</sub> O <sub>2</sub> , 0.05	150	Gummy, soft, tacky
35	E. F. Houghton No. 4			1.0	NH <sub>4</sub> Alg.	50	45		H <sub>2</sub> O <sub>2</sub> , 2	90	Soft and tacky

<sup>a</sup> Allyl lactate maleate.<sup>b</sup> Ammonium alginate (Supericoid).<sup>c</sup> Plus 0.2 ml. of allyl acrylate.<sup>d</sup> Insoluble in acetone or toluene.<sup>e</sup> Reduced during polymerization; temperature of mixture was approximately 75° C.; films were prepared by pouring a sample of emulsion onto a glass plate and allowing the water to evaporate.

variable. Fryling (6) made interesting observations regarding changes in pH during emulsion polymerization.

Use of extremely small quantities of emulsifiers was not studied, but polymerization occurred less readily when Triton K60 was used in low concentration with hydrogen peroxide as catalyst. This is in agreement with the observations of Fryling (6).

Unless monomers (usually about 2% of the quantity used in the experiment) were removed, the emulsions had an objectionable odor. In many instances, steam was passed through the emulsions at the end of polymerization to remove residual monomers and improve the odor.

### CONTROL OF VISCOSITY

Viscosity influences the ease with which both resin emulsions and solutions can be applied. The viscosity of resin solutions increases so rapidly with increase in resin concentration that the resin content must be kept low enough for convenient application. On the other hand, aqueous resin dispersions usually are fluid, even when the resin content is 50% or even higher. Data supplied by Jackson (8) illustrate the differences between the viscosities of aqueous dispersions and ethyl acetate solutions of an acrylic resin (Table V).

The viscosity of resin solutions can be controlled easily by changing the resin concentration (Table V) or the solvent, but the viscosity of resin emulsions cannot be controlled by these methods. Since resin emulsions are ordinarily fluid, several agents, including methylcellulose (1), have been added to increase the viscosity and facilitate brushing, spraying, or calendering (7). Although these agents are useful for some purposes, some of them have distinct disadvantages. Methylcellulose, for example, cannot be added before polymerization because its solutions are coagulated by elevated temperatures. Moreover, it is moderately soluble in cold water, and films containing methylcellulose would be expected to have decreased water resistance.

During this study a simple and effective method for preparing acrylic resin emulsions of almost any desired viscosity was found. This consists in adding a casein preparation and a water-soluble alginate before polymerization. The casein and alginate have a synergistic effect on

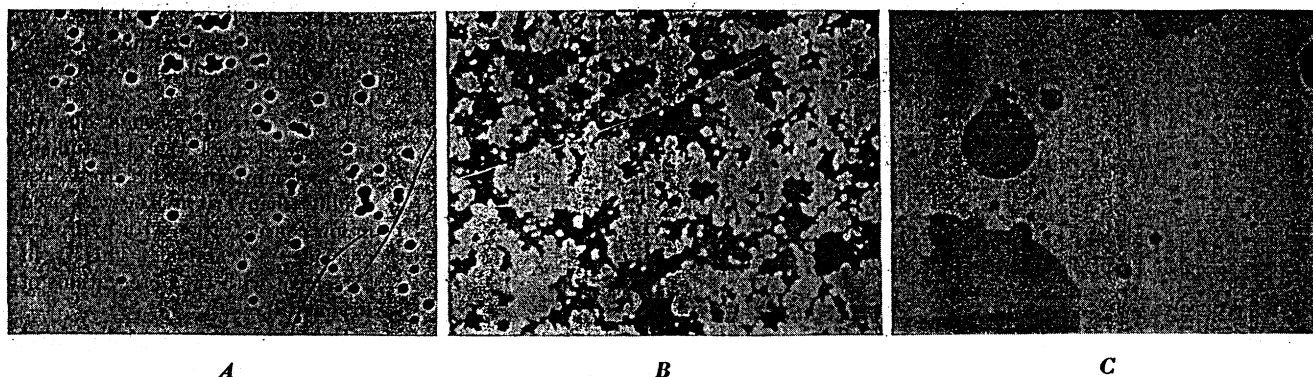


Figure 1. Electron Micrographs of Methyl Acrylate Polymer Emulsions

viscosity, and small amounts of these two agents, when used together, produce highly viscous emulsions.

The emulsions were made with the equipment and technique described early in the paper. After polymerization was completed, the emulsions were allowed to cool to room temperature with stirring and were then poured into glass bottles to stand

overnight before the viscosity was measured. The samples were shaken gently, and the viscosity was determined with a Brookfield Synchro-lectric viscometer at 6, 12, 30, and 60 revolutions per minute. The emulsions were thixotropic and, in some instances, considerably thinned by agitation. The accuracy of the viscometer was checked periodically with oils of known viscosity supplied by the National Bureau of Standards. No attempt was made to maintain an accuracy higher than 10% of the scale value of the instrument.

It has been claimed (4) that casein retards the polymerization of some monomers. Results of the present work indicate that this effect causes no real difficulty. Of the various casein preparations studied—Protovac 8979, rennet casein, and acid casein—satisfactory results were obtained only with Protovac 8979.

Although emulsifiers other than Tergitol Penetrant No. 4 were given little attention, Triton K60 and Daxad No. 11 were used satisfactorily (in combination with ammonium alginate and modified casein) to produce viscous, acrylic resin emulsions. Nacconol seemed less suitable.

The few observations made of the pH value indicated that the emulsions were never highly acidic or basic. This might have been partly due to a bufferlike action of the casein. In some instances a mixture of sodium borate and sodium hydroxide was added before polymerization without any important noticeable effect.

The size of resin particles in several methyl acrylate polymer emulsions was determined by examination of electron micrographs. Representative fields are shown in Figure 1. The particle size in some emulsions was rather uniform, most diameters lying in the range 0.1 to 0.4 micron (Figure 1A). B illustrates the aggregation of spherical particles of the same emulsion to form chains, clusters, and networks. In many cases coalescence was incomplete, as evidenced by density variation over the image of aggregates and especially by the circular outline of particles near the periphery. C shows the tremendous variability in particle size in one of the resin emulsions. Particles ranged from less than 0.1 to more than 7 microns in diameter.

Films were prepared from some of the emulsions (casein and ammonium alginate type) by spreading the emulsion on a pane of glass and allowing the water to evaporate. The films prepared from foamy emulsions had bubbles, but this difficulty could be avoided by adding a small amount of *n*-hexanol or *n*-octanol either before or after the emulsion polymerization. Because of

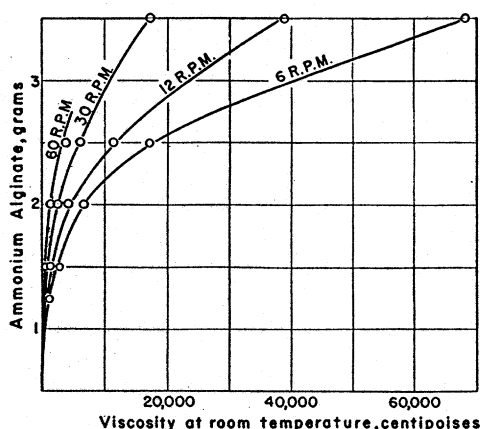


Figure 2. Effect of Ammonium Alginate on Viscosity

TABLE III. EMULSION POLYMERIZATION OF ETHYL ACRYLATE<sup>a</sup>

Expt. No.	Emulsifier	Grams	Water, Ml.	Ethyl Acrylate, Grams	Ammonium Persulfate, Mg.	Time, Min.
1	Tergitol Penetrant No. 4	3	300	200	3.0	80
2	Tergitol Penetrant No. 4 paste	4	400	200	5.0	50
3	Triton 720	2.5	400	130	5.0	50
4	Triton 720	1.0	400	200	5.0	50
5	Tergitol Penetrant No. 4	2.0	1600	800	5.0	100
6	Triton 720	4.0	6000	3000	40.0	180
	Tergitol Penetrant No. 4	14.0				
	Triton 720	30.0				
	Tergitol Penetrant No. 4 paste	60.0				

<sup>a</sup> Refluxed; temperature 82–91° C.

TABLE IV. EMULSION POLYMERIZATION OF METHYL ACRYLATE

Expt. No.	Ammonium Alginate, Grams	Protovac 8979, Grams	Other Agents, Grams	Water, Ml.	Methyl Acrylate, Grams	Ammonium Hydroxide, G.	Ammonium Persulfate, G.	Time, Hr.
1	1.25	10.0	Tergitol Penetrant No. 4, 5.0	300	150	0.9	0.125	2 1/2
2 <sup>a</sup>	6.25	35.0	Tergitol Penetrant No. 4, 23.5	1500	750	10.0	0.112	2 1/2
3 <sup>b</sup>	0.4	3.0	Tergitol Penetrant No. 4, 3.2	140	73	0.9	0.290	8 1/2
4	1.5	..	l-Ascorbopalmitate, 1.0	175	125	1.0	0.120	4 1/2
5	..	..	Ursolic acid, 1.5; Pectinate H-69 <sup>c</sup> , 1.0	200	150	1.5	..	5
6	4.0	..	E. F. Houghton No. 1, 4.0	250	250	3.0	0.800	2 1/4

<sup>a</sup> 15 ml. *n*-hexyl alcohol also used.

<sup>b</sup> 0.3 g. Sudan Red BBA dissolved in monomer.

<sup>c</sup> Palmitate of ascorbic acid (14).

<sup>d</sup> 13 ml. H<sub>2</sub>O<sub>2</sub>.

<sup>e</sup> Apple pectin after demethylation with acid.

TABLE V. VISCOSITIES OF COMPARABLE SOLUTIONS AND EMULSIONS OF POLYMERIZED ETHYL ACRYLATE\*

Concn. of Polymer, %	Viscosity, Minutes	
	Ethyl acetate soln.	Aqueous dispersion
5	17.2	12.2
10	64.6	12.4
20	No longer measurable	12.7
25	Ditto	12.8
50	Ditto	20.3

\* Viscosities were determined at 20° C. in the No. 4 Ford cup.

TABLE VI. EFFECT OF AMMONIUM ALGINATE ON VISCOSITY OF METHYL ACRYLATE EMULSIONS\*

Expt. No.	Ammonium Alginate <sup>b</sup> , Grams	Brookfield Viscosity, Centipoises			
		6 r.p.m.	12 r.p.m.	30 r.p.m.	60 r.p.m.
1	0.25	Too low	3	6	8
2	0.75	40	40	35	32
3	1.25	910	615	370	260
4	1.75	3,500	2,250	1,200	780
5	2.00	6,400	4,150	2,200	1,440
6	2.50	17,000	10,800	5,800	3,750
7	3.50	68,000	39,000	17,280	Above range of spindle

\* Ingredients other than ammonium alginate: water, 350 ml.; Protovac 8979, 7 g.; Tergitol Penetrant No. 4, 5 g.; methyl acrylate, 250 ml.; dodecyl mercaptan, 1 ml., and hydrogen peroxide. Viscosity of water at 20° C. is 1.0050 centipoises.

<sup>b</sup> Superlloid.

excellent adherence, it was difficult to remove some of the films from the glass surface. The films could be removed easily, however, after soaking in hot water.

Water resistance of some of the films was determined by suspending a strip of the film in water for several days, noting the increase in weight, and observing the effect of the water on the appearance and strength of the specimen. Resistance to water was not satisfactory, but the methyl acrylate and methyl acrylate-acrylonitrile films were little affected by hydrocarbons containing less than 50% aromatics.

**EFFECT OF AMMONIUM ALGINATE.** As mentioned above, the greatest increase in viscosity resulted when both the alginate (Superlloid) and casein preparation (Protovac 8979) were used. Increasing the proportion of alginate, however, was more effective in increasing the viscosity than using larger amounts of the modified casein (Table VI and Figure 2). When the quantity of ammonium alginate was increased from 0.25 to 3.5 grams, the viscosity of the resulting emulsions was raised from approximately 2 to 68,000 centipoises, a 34,000-fold increase. This remarkable increase in viscosity, however, depended on the modified casein, since fluid emulsions (2 to 5 centipoises) resulted when the casein preparation was omitted. It is apparent from Figure 2 that the greatest effect on the viscosity was caused by increasing the quantity of ammonium alginate from 2 to 3.5 grams (0.84 to 1.47% by weight of the methyl acrylate polymerized).

**EFFECT OF MODIFIED CASEIN.** The modified casein (Protovac 8979) also increased the viscosity of the emulsions (Figure 3).

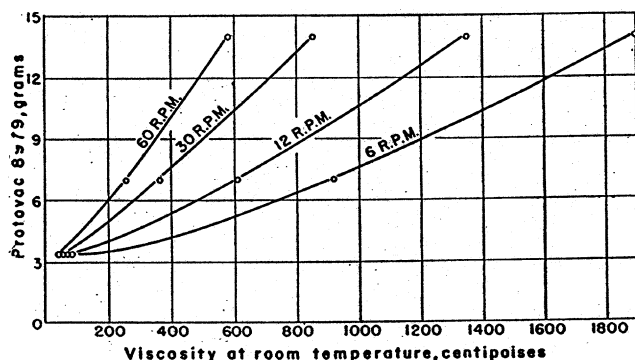


Figure 3. Effect of Protovac 8979 on Viscosity

Less than approximately 3 grams had little effect on the viscosity, but the viscosity increased greatly when the quantity was increased from 3.5 to 14 grams (1.47 to 5.9% by weight of the methyl acrylate polymerized).

The quantity of the casein preparation required to produce viscous emulsions was appreciable; hence the influence of the casein on the properties of the resin films deposited from the emulsions merits consideration. The films obtained from the resin emulsions contained approximately 1.5 to 6.0% of the modified casein. The casein decreased tack and increased the water resistance of the films, but the most noticeable effect was the increased tenacity with which these films adhered to smooth surfaces. Hence, the over-all effect of the casein preparation in the resin film appears beneficial. Butler (3) stated that as much as 10% of Protovac 8979 in films of ester resin does not affect water resistance or durability.

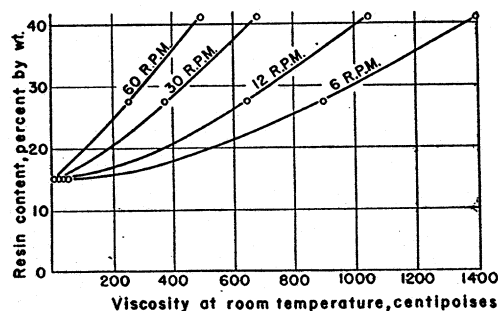


Figure 4. Effect of Resin Content on Viscosity of Polymethyl Acrylate Emulsions (Brookfield)

**EFFECT OF RESIN CONCENTRATION.** Unlike the acrylic resin emulsion (Table V) described by Jackson (8), the viscosity of the emulsions prepared with peptized casein and ammonium alginate was dependent on the resin content, particularly when the resin content was higher than 15% (Figure 4). This fact may be attributed to the alginate and modified casein, since emulsions containing as much as 55% of acrylic resins were fluid in the absence of these agents. Other ingredients used in the experiments shown in Figure 4 were 150 ml. water, 0.4 gram ammonium alginate, 3.0 grams Protovac 8979, 3.2 grams Tergitol Penetrant No. 4, and hydrogen peroxide.

#### ACKNOWLEDGMENT

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# EMULSION POLYMERIZATION OF ACRYLIC ESTERS

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Effects of various agents on the emulsion polymerization of acrylic esters are described, and directions are given for preparing several types of resin emulsions. When emulsion polymerization is used merely to convert monomeric acrylic esters into polymers or copolymers of relatively high molecular weight, Tergitol Penetrant No. 4 and ammonium persulfate can be used satisfactorily as emulsifier and polymerization catalyst, respectively. The resulting emulsion is only moderately stable and can be coagulated readily by the addition of aqueous solutions of sodium chloride, acetic acid, or mixtures of the two. Triton K60 and hydrogen peroxide also can be used conveniently to produce emulsions of only moderate stability. Emulsions remarkably stable to electrolytes (but not to mechanical agitation or solvents such as acetone and ethanol) can be made with Triton 720 as the emulsifier. Triton 720 and Tergitol Penetrant No. 4 can be used together in various proportions to produce emulsions of almost any desired stability to electrolytes. Stable emulsions suitable for brushing and spraying can be prepared with several combinations of agents. The combination used frequently for this purpose is E. F. Houghton No. 1, ammonium alginate, ammonium hydroxide, and ammonium persulfate. The viscosity of acrylic resin emulsions can be controlled over a wide range by using various quantities of ammonium alginate, modified casein, and Tergitol Penetrant No. 4. Films obtained from these emulsions adhere well to smooth surfaces.

**B**ECAUSE of several inherent advantages, aqueous dispersions of resins, including the acrylic resins (12), are being used to an increasing extent for coating cloth, leather, and other materials. Advantages of aqueous dispersions include ease of application, rapid drying, and freedom from the fire and toxicity hazards that ordinarily accompany the use of resins dissolved in organic solvents.

During investigations in this laboratory concerned with the polymerization and copolymerization of acrylic esters and the production of stable resin emulsions, considerable information was obtained on the use of various emulsifiers and auxiliary agents in the emulsion polymerization of acrylic esters. Some of the results are given in the present paper. The first part of the paper describes various combinations of emulsifiers and polymerization catalysts for preparing acrylic resin emulsions of moderate or high stability; the latter part gives methods for preparing emulsions of almost any desired viscosity. The general properties, advantages, and applications of resin emulsions have been discussed at length elsewhere (2, 4, 9, 10, 11, 13).

The emulsions were prepared in a round-bottom, three-neck Pyrex flask fitted with glass-ground joints for a condenser, water-sealed glass stirrer, and thermometer well. Water and emulsifier were stirred and heated (below 85° C.) in the flask until a smooth dispersion or solution was obtained. The monomer or monomers were then added, and polymerization was induced by heat and catalysts. Hydrogen peroxide (30%) and ammonium persulfate were used as catalysts in many of the experiments. The emulsions were refluxed during the polymerization, and at refluxing temperature a period of 30 minutes to several hours was usually required. With half-moon or paddle-type stirrers operated at 100 to 150 revolutions per minute, emulsions with particle size as

small as 0.05 micron in diameter were made without incorporation of air. The yield of polymer was almost quantitative. In some cases steam was blown through the emulsion at the end of the polymerization to remove unchanged monomer. The temperature rose during the polymerization from about 72° to 82° C. and from 82° to 92° C. when methyl acrylate and ethyl acrylate, respectively, were the monomers. Hence the course of the polymerization could be followed roughly by noting the temperature. The polymerizations were followed in some instances by observing changes in the refractive index, density, and solids content.

Emulsion polymerization can be carried out more satisfactorily if, in addition to suitable emulsifiers and catalysts, pure monomers and critical conditions of temperature and catalyst concentration are used. The monomer should be free of inhibitors or regulators or their amount and effect should be known. The monomer should be freshly distilled (under vacuum if high boiling) or, when storage is unavoidable, kept under conditions unfavorable for peroxide formation. Removal of inhibitor with dilute sodium hydroxide (1 or 2%) should be followed by several washings with distilled water, dilute sulfuric acid (0.01%), and twice again with distilled water. Removal of inhibitor from methyl and ethyl acrylate in this manner causes a considerable loss of monomer.

The amount of ammonium persulfate required to initiate polymerization depends largely on the temperature. Only traces of catalyst are needed under refluxing conditions (approximately 72° for methyl acrylate and 82° for ethyl acrylate), but much larger quantities are needed at somewhat lower temperatures. Polymerization may not occur in several hours with the same amount of catalyst if the temperature is as little as 0.5° below refluxing. Too much catalyst causes a vigorous reaction, violent refluxing, and, in some instances, coagulation of the emulsion. When only traces of catalyst are used at gentle refluxing temperature, polymerization proceeds smoothly, yielding a polymer of high molecular weight; little or no additional heating is required; and the polymerization can be controlled by the rate of addition of the catalyst. A steam bath is more satisfactory than a water bath for this type of polymerization.

The benefits of carrying out the emulsion polymerization of monomers and monomer mixtures at refluxing temperature are so outstanding that some feature of refluxing other than temperature seems important. If it is assumed that most of the polymerization occurs in the aqueous phase, refluxing might be beneficial because of increased solubilization of the monomer or the increased rate at which the monomer is transported from the oil phase into and throughout the aqueous phase.

Fryling (5) described suitable laboratory methods for preparing resin emulsions from small quantities of monomers and for following the course of the polymerization.

## EMULSIONS OF MODERATE STABILITY

The emulsifiers listed in Table I formed dispersions of moderate stability without auxiliary agents or other emulsifiers. Hydrogen peroxide (30%), which has the advantage of being essentially neutral and decomposing into water, was used conveniently as a catalyst in these initial experiments. In a few instances, when it

TABLE I. POLYMERIZATION OF METHYL ACRYLATE WITH ONE EMULSIFIER<sup>a</sup>

Expt. No.	Trade Name	Emulsifier Type (8, 15)	Grams	Water, Ml.	Methyl Acrylate, Ml.	H <sub>2</sub> O <sub>2</sub> , Ml.	TiB, Min.
1b	Triton W-30	Sulfated aromatic ether alcohol	.9	50	45	0.5	60
2c	Triton K-60-S	Quaternary ammonium salt	4.5	250	250	2	50
3c	Nacconol NRSF	Sodium alkyl aryl sulfonate	.9	50	45	0.5	60
4b	Gardinol LS	Fatty alcohol sulfate	.9	50	45	0.5	45
5c	Aquasol AR-75%	Sulfonated castor oil	.9	50	45	0.5	60
6c	Tergitol Penetrant No. 4	Sodium salt of higher secondary alkyl sulfate	.9	50	45	0.5	45
7b	.....	Glyceryl monostearate	.9	50	50	0.5	...
8c	E. F. Houghton No. 1	.....	.9	60	40	0.25	30
9b	E. F. Houghton No. 3	.....	1.8	60	40	0.5	60
10c	E. F. Houghton No. 4	.....	.9	60	40	0.5 <sup>d</sup>	60
11c	Daxad No. 11	Polymerised Na salts of alkyl naphthalene sulfonic acids	1.0	50	45	2	...
12b	Daxad No. 23	Polymerised Na salts of substituted benzoic alkyl sulfonic acids	1.0	50	45	3 <sup>e</sup>	...
13	Atlas Span 85	Sorbitan trioleate	3.0	50	40	1	...
	Atlas Tween 85	Sorbitan trioleate polyoxyalkylene derivative	2.0				
14	Atlas Span 20	Sorbitan monolaurate	2.0	50	40	1	...
	Atlas Tween 20	Sorbitan monolaurate polyoxyalkylene derivative	2.0				
15	Emulphor ELA <sup>f</sup>	Ethylene oxide condensate with fatty acids	2.0	70	50	4.	150
16	Emulphor ON/	.....	2.0	70	50	4.	105
17/	Igepon T	C <sub>17</sub> H <sub>35</sub> CON—CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na	2.0	70	50	1	10
18	Igepon AP extra	Na sulfonate of oleic acid ester of aliphatic compound	2.0	70	50	1	240
19/	Nekal BX	Sodium alkyl naphthalene sulfonate	2.0	70	50	1	30
20/	Nekal BX	Sodium alkyl naphthalene sulfonate	2.0	70	50	2	35
21	NH <sub>4</sub> Alginate	Ammonium alginate	1.0	50	40	1	20
22	Pectinate H-69	Acid-demethylated pectin	1.4	70	50	0.5	20
23	Protovac 8979	Modified casein	5.0	70	50	0.5	11
24	Nekal A	Sodium alkyl naphthalene sulfonate	1.0	70	50	0.3	6

<sup>a</sup> The mixture was refluxed (temperature of mixture, 75° C.) until polymerisation was virtually complete.

<sup>b</sup> A large amount of polymer separated during the polymerisation.

<sup>c</sup> Emulsions were satisfactory except for brushing or spraying.

<sup>d</sup> 0.5 gram benzoyl peroxide was also used.

<sup>e</sup> Heating reduced emulsifying action.

<sup>f</sup> A small amount of polymer separated during polymerisation.

appeared that hydrogen peroxide alone was not sufficiently effective, a small amount of benzoyl peroxide was added. Ammonium hydroxide, Houghton No. 2<sup>1</sup>, Triton NE, Emulphor AG, and Nekal RU appeared to inhibit the polymerization of methyl acrylate under conditions similar to those shown in Table I.

The emulsions obtained with single emulsifiers (Table I) were not stable enough for brushing or spraying. Optimum conditions for each emulsifier were not determined, and it is possible that different concentrations and conditions would have given improved emulsions. Emulsions of only moderate stability are desirable for some purposes, and some of the formulas of Table I could be used to advantage under such circumstances. Triton K60S (experiment 2) has been used conveniently in this laboratory many times in converting acrylic esters into resins of relatively high molecular weight; in these experiments the emulsions were coagulated by the addition of dilute solutions of sodium chloride, acetic acid, or mixtures of the two.

When used under the conditions shown in Table I, the following materials appeared unsuitable as emulsifiers in the polymerization of methyl acrylate: Triton W-30, Gardinol LS, glyceryl monostearate, Houghton No. 3, Daxad No. 11, Atlas Span 85 + Atlas Tween 85, Atlas Span 20 + Atlas Tween 20, Igepon AP extra, ammonium alginate, Pectinate H-69, Protovac 8979, and Nekal A. These agents were not studied thoroughly, however, and excellent results might have been obtained with other monomers under other conditions, or when used in conjunction with other emulsifiers.

#### STABLE EMULSIONS

Some of the emulsifiers that had given promising results in the earlier experiments (Table I) were used in later experiments with other agents. Emulsions stable enough for brushing and spraying were obtained with certain combinations of agents (Table II). It was not demonstrated that these combinations would function satisfactorily with all monomers, but stable emulsions were obtained when methyl acrylate was polymerized alone or copolymerized with acrylonitrile or bis-(carballyloxyethyl)maleate (prepared from 2 moles of allyl lactate and 1 mole of maleic anhydride). The combination used most often consisted of Houghton No. 1, ammonium alginate, and ammonium hydroxide (experiments 1 to 5 and 18 to 23, Table II, and experiment 6,

<sup>1</sup> Obtained through the courtesy of J. T. Eaton of E. F. Houghton & Company.

Table IV). Ammonium hydroxide had little or no inhibiting effect, possibly because it was partly or totally neutralized by Houghton No. 1.

Triton 720 (sodium salt of aryl alkyl polyether sulfonate) formed emulsions that were remarkably stable to electrolytes (Table III). Although stable when treated with sodium chloride, acetic acid, or hydrochloric acid, the Triton 720 emulsions could be coagulated by mechanical treatment or by the addition of alcohol or acetone. With mixtures of Triton 720 and Tergitol Penetrant No. 4, emulsions of almost any desired stability to electrolytes were prepared (Table III).

#### SELECTION OF POLYMERIZATION CATALYST

Although hydrogen peroxide has certain advantages and was used satisfactorily in many experiments, the ammonium persulfate is preferable as catalyst. With this agent the polymerizations proceeded smoothly, and it was effective in exceedingly low concentrations; polymers of high molecular weight could be prepared easily with traces of it. Presumably potassium and certain other persulfates could be used. Sodium perborate appeared to have no particular advantage. Benzoyl peroxide was active and was used in conjunction with hydrogen peroxide when the latter seemed ineffective.

Ammonium persulfate was not employed with all the emulsifiers shown in Tables I and II, but it was used satisfactorily with Tergitol Penetrant No. 4 and a mixture of Houghton No. 1, ammonium alginate, and ammonium hydroxide. Other examples of the preparation of satisfactory emulsions with ammonium persulfate are given in Tables III and IV. Unlike hydrogen peroxide, ammonium persulfate was unsatisfactory with Triton K60, owing to the formation of a precipitate.

#### MISCELLANEOUS OBSERVATIONS

Of the several agents tried (mineral oil, *n*-octanol, lauryl alcohol, *n*-hexanol, castor oil, and ethanol), *n*-octanol and *n*-hexanol seemed most suitable for preventing foaming. A small amount was added during the polymerization when foaming became excessive.

Dodecyl mercaptan appeared to facilitate control of the rat polymerization, particularly when hydrogen peroxide was used as catalyst.

The effect of pH was not studied thoroughly, and few conclusions were reached regarding the desirability of controlling this